

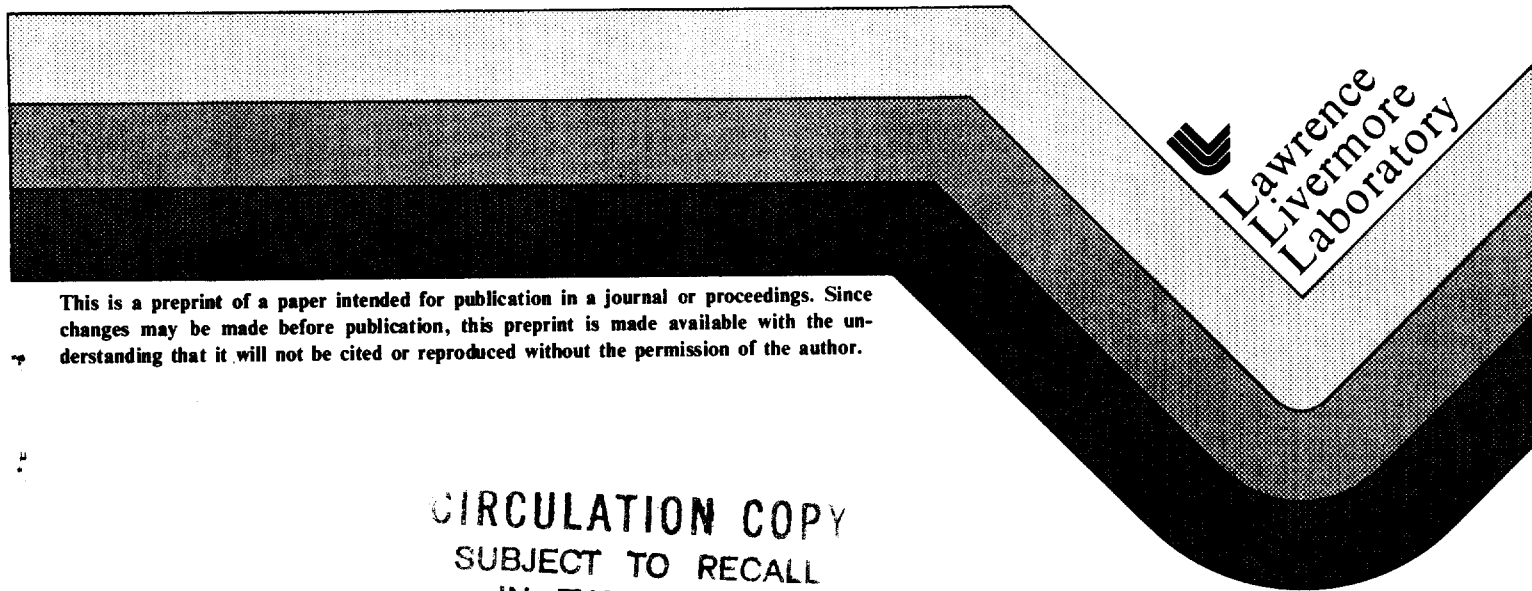
UCRL- 83602  
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POLYMERIC COATINGS EFFECT ON ENERGY AND  
SENSITIVITY OF HIGH EXPLOSIVES

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This paper was prepared for presentation at  
the American Chemical Society Meeting in Houston,  
Texas, March 1980 and for publication in the  
I & EC Product Research & Development Journal.

July 31, 1980



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POLYMERIC COATINGS EFFECT ON ENERGY AND SENSITIVITY  
OF HIGH EXPLOSIVES

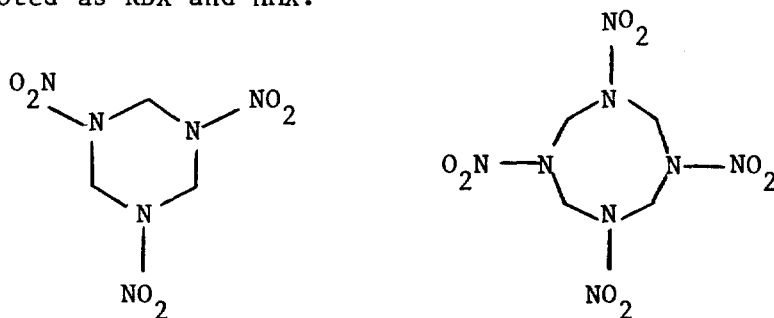
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ABSTRACT

There is a continuing effort at Lawrence Livermore National Laboratory to formulate new plastic-bonded explosives (PBX) with enhanced energy and improved safety characteristics. We have found that these parameters depend mainly upon the polymer or plastic chosen as binder. Typically these materials have five to ten volume percent polymer and the explosive may be treated as a solid coated with a polymeric film. In an effort to determine which properties of a polymer are advantageous here, we have examined in depth three polymers (Kel-F 800, Phenoxy PKHJ, and Kraton G 1650) and an insensitive explosive (1,3,5-triamino-2,4,6-trinitrobenzene (TATB)). We determined mechanical and rheological properties, surface characteristics, and acid-base behavior of the pure materials and composites (PBX). It was found that extensibility, glass transition temperature, Lewis acidity surface wettability of the components of a PBX are governing factors in safety characteristics.

## INTRODUCTION

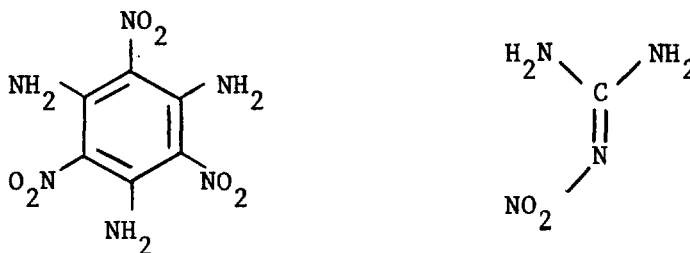
Chemical high explosives (HE) have a continuing and multitudinous role in industrial applications and in the Department of Energy (DOE) complex. Historically, the most common base HEs for DOE applications have been cyclic nitramines denoted as RDX and HMX.



As one might imagine, these explosives are subject to a number of problems related to their sensitivity and stored energy, i.e., shock sensitivity and chemical instability leading to unstable degradation products. These materials, replete with both physical and chemical problems, render it incumbent upon the user to adopt means of stabilizing the materials in order to obtain the maximum safe, useful work from them. For roughly 35 years the most common behavior modifier has been a polymer (with or without a concomitant plasticizer) which acts as a binder for the individual HE particles. The main advantages of the binders are 1) desensitization of the HE to unwanted external stimuli; 2) enhancement of the maximum possible energy which may be extracted from the explosive; 3) the imparting of structural integrity to the PBX composite. Some of the polymers which are utilized as HE binders are fluorocarbon, urethane, and silicone polymers.

It was recognized previously that for the sensitive RDX and HMX compositions, it was necessary to use relatively "soft" (low modulus), rubbery polymers to minimize shock sensitivity because high modulus binders yield stiff, crack-susceptible, highly sensitive composites. To incorporate these binders it was necessary to exclude enhancement of energy and the ability to design structural parts from these Polymer Bonded eXplosives (PBX) due to

their compliant makeup. Recently, however, intense interest has arisen in two chemicals that were initially synthesized long ago, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and nitroguanidine (NQ).



These materials are possessed of extreme insensitivity and have spawned a new generation of PBXs of exceptional stability and safety characteristics. Both materials consist of infinite, essentially two-dimensional planar arrays of intermolecular hydrogen-bonded molecules (Cady and Larson, 1965; Bryden et al., 1956). In addition to the intermolecular hydrogen bonding, similar intramolecular hydrogen bonding contributes to the overall thermal, chemical and physical stability of the HEs. The two dimensional covalent and hydrogen bonded frameworks essentially preclude bonding in the third dimension so that, despite weak Van der Waals interactions perpendicular to the planes of bonding, the planes are relatively free to move with respect to one another. This planarity also results in highly anisotropic thermal expansion (Kolb and Rizzo, 1978, 1979) and, in the case of TATB, permanent growth (Rizzo et al., 1978) of pressed powder and pressed PBXs can occur.

While the anisotropy of the insensitive HEs presents certain design problems, these materials represent the first real opportunity to assess the effect that the polymer has on the resultant mechanical and physical properties of the composite PBX. To date a very small amount of work has been done to generate fundamental data germane to a better understanding of surface interactions between HE particles and polymer binders and how they influence PBX properties (Hammon and Althouse, 1976; Yee, 1978). Typically a PBX composite may consist of from 80 to 97 volume percent explosive, with the remainder being polymer. For the purposes of this study, we will ignore plasticizers, coupling agents and UV stabilizers all of which have been utilized in explosive composites at one time. With the necessary safety

considerations and constraints inherent in most RDX and HMX PBXs absent in TATB formulations, it is possible to look more carefully at the role polymer properties play in the mechanical and physical properties of resultant composites.

Toward this end, we have initiated a program at Lawrence Livermore National Laboratory (LLNL) to assess the relative contribution of binder properties to ultimately safe, structurally sound PBXs. The work presented here will describe the mechanical and dynamic mechanical properties of several polymers of choice, TATBs and PBXs. In addition, we describe the results of initial investigations on the surface energies of the components and PBXs. In close association with the surface studies, we have conducted an investigation into the relative Lewis acidity/basicity of polymers, HEs and PBXs. With the data thus assembled it is possible to paint a relatively complete picture of the mechanical, chemical and surface characteristics of several binders and TATBs. With similar data on hand for the composite PBXs, it is then possible to determine the extent of polymer participation and influence on the final composite properties.

## EXPERIMENTAL

### Materials

Each of the polymers used as binders (3M Kel-F 800, vinylidene-fluoride-chlorotrifluoroethylene copolymer, Shell Chemical block copolymer Kraton G 1650 poly(styrene-ethylenebutylene-styrene) and Union Carbide Phenoxy resin PKHJ) are adsorbed onto both thermally treated and untreated TATB in three solvents (THF,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ). TATB was thermally treated in an oven for 6-12 weeks at  $120^\circ\text{C}$  to assess thermal aging effects on the surface properties of the material. The TATB used is a normal production grade from Cordova Chemical Company with a surface area of  $0.792 \text{ m}^2/\text{g}$ . Other TATB powders studied are Rocketdyne materials, one a chlorine-free material with a surface area of  $0.502 \text{ m}^2/\text{g}$  prepared by aqueous nitrobenzene amination and one a micronized chlorine-free material with a surface area of  $4.575 \text{ m}^2/\text{g}$ .

The composites chosen for investigation all consist of TATB as the HE in various percentages (Table I) and Kel-F 800 (denoted BB), Phenoxy resin PKHJ (denoted DI) or Kraton G 1650 (denoted DK, DN, or DU) as binders.

### Methods

For the delineation of acid-base characteristics, solutions of 1.0 to 1.5 g of polymer in 100 mL of solvent were equilibrated with a weight of TATB filler about equal to the weight of the polymer. After 15 minutes, the suspension was centrifuged and a 10 mL aliquot of the clear supernatant liquid was evaporated to dryness, then dried for 48 hours at 120° to 130°C in a vacuum oven. The weight of residual polymer was compared with suitable blanks. For contact angle measurements, small pellets of TATB powder or TATB PBX were pressed. The contact angles for a series of reference liquids on the smooth pellets were measured using a reflective goniometer. The liquids chosen were formamide, bromonaphthalene, tetrabromoethane, benzyl alcohol, hexachloropropene, chlorobenzene and tetrachloroethylene. The critical surface tensions for the liquids were extracted from Zisman's data (1964). Critical surface tension was determined using the method of Zisman (1964). Polymer surfaces studied were either pressed (Kel-F, Phenoxy) or cast films (Kraton).

Mechanical testing of the polymers, TATBs and TATB PBXs was conducted on an Instron Universal Test machine. A constant crosshead speed of 0.005 cm/min. was used. The polymer samples were compression molded and the TATB and TATB PBXs were machined to specification. Dynamic mechanical properties of the materials were examined on a Rheometrics Mechanical Spectrometer (RMS) using a forced torsion fixture.

### RESULTS AND DISCUSSION

The surface characterization will be discussed first so that the surface properties which are delineated may be used to assist in an analysis of the mechanical results. For example, if a polymer chosen as a potential binder

has both a fairly high surface energy as well as a number of acidic sites, the ideal explosive should have a roughly equivalent surface energy and a complementary basicity. If such is not the case, e.g., if the HE is also somewhat acidic or of low surface energy, then the tenacity with which the polymer adheres to the HE filler is lacking. One would then find that the binder is not actually "binding", it is merely acting as a non-adhering matrix or network into which the filler may disperse. The resultant mechanical properties and behavior would then be expected to approximate those of the component present to the greatest extent, in this case the explosive.

### Surface Characterization

Fowkes has shown that adsorption of polymers from solvents onto the surface of an inorganic solid involves interactions between polymers and solvents and between solvents and inorganic solids (Fowkes and Mostafa, 1978). They were able to demonstrate that acid-base interactions dominate, enabling us here to ultimately study the PBXing process since it too involves a similar system, i.e., there is an interaction between polymer, solvent, and HE filler, probably of the Lewis acid-base type. It should be pointed out that TATB has both acidic ( $-\text{NO}_2$ ) and basic ( $-\text{NH}_2$ ) sites in its molecular framework. These many competing sites of differing activity result in an overall amphoteric character for TATB.

THF,  $\text{CCl}_4$ , and  $\text{CHCl}_3$  were the three solvents chosen because basicity (THF) and acidity ( $\text{CHCl}_3$ ) have been quantified by Drago et al., (1971). The neutral solvent ( $\text{CCl}_4$ ) was Drago's choice as a neutral solvent. Of the three polymers used as binders Kraton G 1650 adsorbed well onto both untreated TATB and thermally treated TATB. This was true regardless of the solvent chosen (Tables II and III).

Kel-F 800 adsorbed well onto both untreated and thermally treated TATB in THF only indicating poor adsorption capabilities in neutral and acidic solvents. Phenoxy PKHJ, however, adsorbed well in both basic and acidic solvents but not in neutral solvent. Thermal treatment of TATB seems to allow



an increase in the adsorption of polymer; thermally treated and untreated materials scarcely differ in their adsorption of the three binders. Those results also serve well to illustrate the consistent adsorption of Kraton G 1650 onto filler in all three solvent systems.

Looking at Tables II and III it is apparent that the Kraton polymer seems unaffected by the relative acidity or basicity of the solvent. In acidic or basic media Phenoxy adsorbs very well onto the surface of TATB. While the Kraton continues to be adsorbed in roughly equivalent amounts even in neutral carbon tetrachloride, the Phenoxy is adsorbed to a considerably smaller degree in  $\text{CCl}_4$ . This behavior indicates then that if a mildly acidic or basic organic solvent is used as the dissolution medium, either Phenoxy PKHJ or Kraton G 1650 provide acceptably high adsorption factors onto TATB. From Tables II and III we can see that both materials are adsorbed onto TATB much more favorably than is Kel-F 800. In THF, Kel-F 800 approaches the adsorption of Phenoxy with both untreated and thermally treated TATB. However, in neutral and acidic media the adsorption of Kel-F 800 is negligible in comparison to those measured for Kraton and Phenoxy (in acidic media).

Four to ten contact angles were measured for each material; TATBs, polymers, and PBXs. The mean angle was used in calculating the critical surface tension values. A plot of  $\cos \theta$  versus  $\gamma_{LV}$ , the known surface tension of liquids, is usually made and the line extrapolated to  $\cos \theta = 1$  (Zisman, 1964). However, since it is a linear plot, it was more convenient to fit the points to a linear regression. These data are presented in Table IV for the polymer binders, pressed TATB powders and pressed PBXs.

A number of conclusions can be drawn on the basis of these results. The first is that untreated TATB PBXs are virtually indistinguishable in terms of surface energies. Within experimental constraints these materials are all relatively low surface energy materials that show no variation on changing binders. The second conclusion is that the block copolymer Kraton G 1650 is a lower surface energy material than either Kel-F 800 or Phenoxy which are indistinguishable in terms of surface activity. This is not surprising in

view of the fact that there are active pendant hydroxyl groups in the linear epoxy chains and active halogen atoms (Cl and F) in the Kel-F 800 chains. Kraton however is a block copolymer with polystyrene endblocks and a poly(ethylene-butylene) midblock: less inherent surface activity would be expected. Another conclusion that may be drawn from the critical surface tension data is that, not unexpectedly, the surface characteristics of the PBX more closely approximate those of the HE than of the polymer. The fact that the HE is present at approximately 95 weight percent in the PBXs is insufficient to ensure a close similarity to the HE surface itself if all particles are uniformly coated. The above result negates the contention that each HE particle is uniformly coated with at least a monolayer of binder.

#### Mechanical Behavior

In the DOE complex, the uses of PBXs are quite varied but, whatever the use, the materials are expected to exhibit some structural integrity. Acid-base interactions between filler and polymer would be expected to enhance mechanical characteristics (Marmo et al., 1976). One would hope that, ideally, adsorption of the binding polymer (to the exclusion of solvent) onto the HE surface would result in uniform coating of the particles. Such was seen not to be the case (vide supra). A further hope, that acid-base interactions may enhance tensile and compressive properties, will be examined here. TATB itself is a weak, non-structural material. The incorporation of a binder through a classical PBXing process (coating of the polymer onto explosive particles in a non-miscible water/organic solvent system) does indeed enhance both tensile and compressive properties (Tables V and VI). However, taking the result that Kraton is the binder which most easily interacts with TATB in all media, we would expect that the tensile properties of Kraton-bonded TATB would be the best. In fact, of the three PBXs examined, DU is the least strong. This is indicative of other mechanisms being operative. The hard plastic phenoxy resin yields the strongest PBX in both tension and compression.

While surface properties undoubtedly play a major part in mechanical and physical properties of the composites, the binder itself appears to exert more influence on the PBX than its minor constituency would indicate. The ordering of the compressive and tensile strength of the three PBXs is the same: Phenoxy > Kel-F > Kraton. From acid/base studies one would have predicted a relative ordering of Kraton > Phenoxy > Kel-F. The effectiveness of acid-base interactions in improving mechanical properties of post-chlorinated PVC filled with  $\text{CaCO}_3$  has been demonstrated (Marmo et al., 1976). However it may be that in our very highly filled polymer systems,  $T_g$  and modulus are as critical to the PBX properties as is surface activity (Table VII). The relative inactivity of the TATB surface as compared to the highly acidic silica or basic calcite (Fowkes and Mostafa, 1978) may be responsible for the seemingly minor part surface activities play in PBX mechanical behavior here.

#### ACKNOWLEDGEMENTS

The authors would like to thank the following members of the Chemistry Department; Don Breithaupt, D. Mark Hoffman, and James Humphrey for invaluable experimental assistance and mechanical test data; H. George Hammon and Harry F. Rizzo for their continual encouragement and assistance.

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. This work was presented at the 179th National Meeting of the American Chemical Society, Houston, Texas, March 1980, Division of Plastics and Organic Coatings.

TABLE I

## COMPOSITIONS OF TATB PBXs INVESTIGATED

<u>PBX</u>	<u>BINDER</u>	<u>WT%</u>		<u>VOL%</u>		
		<u>HE</u>	<u>BINDER</u>	<u>HE</u>	<u>BINDER</u>	
BB	Kel-F 800	92.5	7.5	92.8	7.2	
DI	Phenoxy	96.3	3.7	94.0	6.0	
DK	Kraton	96.3	3.7	92.5	7.5	
DN, DU	Kraton	98.5	1.5	97.0	3.0	

TABLE II

ADSORPTION OF POLYMER BINDERS ONTO UNTREATED TATB  
IN THREE SOLVENT SYSTEMS IN G/M<sup>2</sup> OF FILLER SURFACE

<u>Polymer</u>	<u>THF</u>	<u>CCl<sub>4</sub></u>	<u>CHCl<sub>3</sub></u>
Kraton G 1650	1.89 X 10 <sup>-3</sup>	5.42 X 10 <sup>-3</sup>	3.52 X 10 <sup>-3</sup>
Kel-F 800	5.93 X 10 <sup>-3</sup>	7.56 X 10 <sup>-4</sup>	6.31 X 10 <sup>-4</sup>
Phenoxy PKHJ	7.93 X 10 <sup>-3</sup>	2.50 X 10 <sup>-3</sup>	6.30 X 10 <sup>-3</sup>

TABLE III

ADSORPTION OF POLYMER BINDERS ONTO THERMALLY TREATED TATB IN  
THREE SOLVENT SYSTEMS IN G/M<sup>2</sup> OF FILLER SURFACE

<u>Polymer</u>	<u>THF</u>	<u>CCl<sub>4</sub></u>	<u>CHCl<sub>3</sub></u>
Kraton G 1650	$2.31 \times 10^{-2}$	$2.43 \times 10^{-2}$	$2.9 \times 10^{-2}$
Kel-F 800	$4.18 \times 10^{-2}$	$3.40 \times 10^{-3}$	0
Phenoxy PKHJ	$3.55 \times 10^{-2}$	$9.23 \times 10^{-4}$	$3.02 \times 10^{-2}$

TABLE IV  
CRITICAL SURFACE TENSIONS ( $\gamma_c$ ) OF POLYMER BINDERS, PRESSED  
TATB POWDERS AND PRESSED PBXs

<u>Material</u>	<u><math>\gamma_c</math></u>	<u>Material</u>	<u><math>\gamma_c</math></u>
Kraton G 1650	25.7	TATB (Cl-free, micronized)	34.0
Phenoxy	31.4	TATB (Cl-free, micronized, tt)	32.7
Kel-F 800	32.7	DK	36.2
TATB (normal)	36.1	DK (tt)	35.4
TATB (normal, tt*)	34.8	BB	34.5
TATB (Cl-free)	35.2	BB (tt)	32.0
TATB (Cl-free, tt*)	31.7	DI	36.2
		DI (tt)	33.0

\*thermally treated



TABLE V

## TENSILE STRENGTHS OF TATB AND PBXs\*

<u>MATERIAL</u>	<u>STRESS (psi)</u>	<u>STRAIN (%)</u>
TATB	735	0.08
BB	1400	0.34
DI	1590	0.26
DU	930	0.28

\*Ambient temperature.

TABLE VI  
COMPRESSIVE STRENGTHS OF TATB AND PBX\*

<u>MATERIAL</u>	<u>STRESS (psi)</u>	<u>STRAIN (%)</u>
TATB	2000	2.0
BB	3000	2.2
DI	5000	2.2
DN	2600	2.8

\*Ambient temperature.

TABLE VII  
BINDER PROPERTIES<sup>1</sup>

<u>MATERIAL</u>	<u>T<sub>g</sub></u>	<u>MODULUS at 23°C (Pa)</u>
Kel-F 800	31	3.1 X 10 <sup>8</sup>
Phenoxy PKHJ	87	1.1 X 10 <sup>9</sup>
Kraton G 1650	-54(SS), 82(HS) <sup>2</sup>	4.4 X 10 <sup>6</sup>
TATB	33	2.3 X 10 <sup>9</sup>
BB	17	1.3 X 10 <sup>9</sup>
DI	98	2.5 X 10 <sup>9</sup>
DK	-63	1.0 X 10 <sup>9</sup>

1. As determined by RMS at 1 Hz.
2. SS (soft segment), HS (hard segment).

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